



Effects of some carboxylic acids on the Fe(III)/UVA photocatalytic oxidation of muconic acid in water

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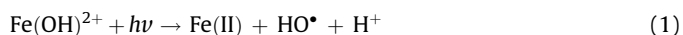
ABSTRACT

Aqueous solutions of muconic acid, taken as model compound, have been exposed to UVA radiation in the presence of Fe(III) and some carboxylic acids: citric, maleic, malic, malonic, succinic, tartaric and oxalic acids. Both black light lamps and solar light were used as a source of UVA radiation. Carboxylic acids studied can be classified into three groups according to the formation or not of photocatalytic or non-photocatalytic active ferricarboxylate complexes. Only carboxylic acids forming ferricarboxylate complexes that absorb in the UVA region are able to improve the photocatalytic oxidation rate of muconic acid since their photolysis likely yields free radicals that act as oxidants. Thus, citric, tartaric, malic and oxalic acids form photoactive ferricarboxylate complexes in the UVA region while malonic acid forms complexes that do not absorb light above 320 nm. Finally, succinic and maleic acids do not form complexes and, as a consequence, their presence do not improve muconic acid oxidation rate. Also, the presence of photoactive ferricarboxylate complexes improves the mineralization rate. Thus, working with black light, after 2 h reaction, TOC conversion increases from about 25% in the absence of carboxylate complexes up to approx. 48 and 75% in the presence of tartrate and oxalate complexes, respectively. The results are even better when solar light is used since total mineralization is reached after 2 h treatment. In this case, a linear correlation between muconic acid half life and 365 nm average intensity of solar radiance was observed. Fe(III)/UVA photocatalytic oxidation resulted to be more effective than TiO₂/UVA photocatalytic oxidation at the conditions applied in this work.

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1. Introduction

Some metal or metal oxides irradiated with UVA–visible light constitute a natural photocatalytic process to decontaminate water. Thus, TiO₂ or Fe(III) with UVA light are usual examples of photocatalytic processes very used in multiple laboratory works. Among these processes, the Fe(III)/UVA process seems to present more advantages because of the abundance of iron salts in the water environments and its easy removal from water once used. Main characteristic of Fe(III) photocatalytic processes is the formation of hydroxyl radicals in the photolysis of Fe(OH)²⁺ at pH between 2.5 and 4 [1] through reaction (1). The process can then be classified as an advanced oxidation process.



The efficiency of this photocatalytic process has already been observed to remove from water compounds such as pesticides [2,3], surfactants [4,5], phenols [6,7] among other [8]. However, the quantum yield of this photolytic process and, hence, its capability to increase the oxidation rate, can be improved with the presence of organic matter able to complex Fe(III). Thus, literature reports that the presence of carboxylic acids such as oxalic, citric or tartaric acids with Fe(III) and UVA radiation improves the water elimination rates of organics such as dyes [9–11], herbicides [12–14], benzene [15] and other hydrocarbons [16]. The reason of this is due to the formation of ferricarboxylate complexes that photolyse to yield free radicals with a quantum yield higher than that of reaction (1).

In this work, the Fe(III)–carboxylate/UVA photocatalytic system is studied to remove muconic acid from water, an intermediate compound of the oxidation of phenols and other aromatic compounds [17–22]. The process has been followed in the presence of different carboxylic acids and with UVA radiation from black light lamps or from solar radiation. The aims of the work were to observe the degree of mineralization achieved and establish some relationship between the nature of carboxylic acids and photocatalytic oxidation rates.

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2. Experimental

2.1. Products, experimental setup and procedure

t-t-Muconic acid (E,E-2,4-hexadienedioic acid) was obtained from Sigma–Aldrich, the rest of carboxylic acids come from Merck and $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ was from Alfa-Aesar. Powdered P25 TiO_2 was directly obtained from the manufacturer, Degussa AG, Germany. All reagents were used as received. Most of reactions were carried out in a 4-L Pyrex glass cylindrical reactor equipped with magnetic agitation and a bubble tube for feeding air. Two 15 W black light lamps (HQPower Lamp15TBL) were situated outside the reactor at 4 cm distance from the reactor walls and at opposing sides. These lamps emitted between 350 and 400 nm with a maximum emission centered at 365 nm radiation. All the system (reactor and lamps) was inside a wooden box to avoid ambient light interferences. The experiments were run as follows: first, 3 L of an aqueous solution, at the prefixed pH (buffered with 0.03 M $\text{HClO}_4/\text{ClO}_4^-$) and known concentrations of muconic acid and another carboxylic acid (when needed), were charged to the reactor; second: air bubbling at a rate of 40 L h^{-1} was fed; third: the lamps were turn on; and fourth: about 20 min later (time to allow lamps work steadily) a known volume of the aqueous solution of Fe(III) was added.

Solar light experiments were carried out in 30 mL borosilicate glass tubes situated at an angle of 40° with respect to the horizontal (according to the latitude of Badajoz city, Spain). These experiments were conducted from October 2006 to July 2007 starting midday (see Section 2.2).

In the case of reactions in the cylindrical reactor, samples were withdrawn at regular intervals while in solar photocatalysis reactions each glass tube was a sample of reaction. In all cases, the aqueous solutions were prepared with Millipore Milli-Q water. Fe(III) solutions were daily prepared and used immediately afterwards.

2.2. Analytical determinations

Muconic acid (MUC) concentration was determined after sampling by HPLC. Previously, the remaining oxidant species were removed with sodium thiosulphate. HPLC analysis were made in a 15-cm long, 0.4 cm i.d. Kromasil C18 column with acetonitrile–water (15/85 v/v) with 0.1% phosphoric acid as mobile phase (flow rate: 1 mL min^{-1}). Detection was made at 264 nm.

Total iron concentration was determined by the ferrozine method [23] that, briefly, consisted in the reduction to Fe(II) and further formation of a violet complex with the ferrozine reagent (molar absorptivity at 565 nm: $27044 \text{ M}^{-1} \text{ cm}^{-1}$, [8]). Fe(II) concentration was determined by the method of Zuo [24] with *o*-phenantroline by measuring the absorbance at 510 nm of the complex (molar absorptivity: $11040 \text{ M}^{-1} \text{ cm}^{-1}$ [8]). Total organic carbon (TOC) was obtained from a 1010 O.I. Analytical TOC analyser.

The intensity of incident radiation coming from the black lamps into the aqueous solution was obtained by actinometry with the ferrioxalate actinometer [25]. A photon flow per unit volume of $2.44 \times 10^{-7} \text{ Einstein s}^{-1} \text{ L}^{-1}$ was determined with both lamps simultaneously working [8]. The intensity of solar radiation at 365 nm was measured with a UVA-365HA Lutron UV meter.

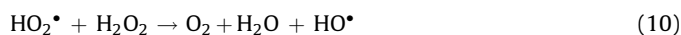
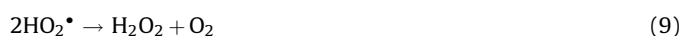
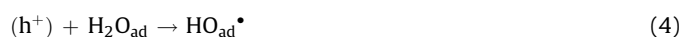
3. Results and discussion

3.1. Use of black light lamps

Since the Fe(III) photocatalytic process could be enhanced by the formation of ferricarboxylate complexes that photolyse to yield

oxidant free radicals, formation of a Fe(III)–muconate complex was first checked. However, absorbance measurements at wavelengths between 250 and 400 nm showed that no ferrimuconate complex was formed.

The first series of experiments were carried with the black light lamps. Muconate does not absorb radiation above 310 nm so direct photolysis when exposed to black light (emission between 350 and 400 nm) is negligible [8]. In a first attempt to establish the importance of Fe(III) photocatalytic oxidation of muconic acid some experiments were also carried out with the powdered TiO_2 photocatalytic system. As it is known, TiO_2 photocatalytic oxidation of organics in water is an extensively investigated process which, in many cases, results in significant organic removal rates. Main reactions of the mechanism of this advanced oxidation process are as follows:



where RX and RX_{ad} mean any non-adsorbed and adsorbed organic compound present in water, respectively.

Then, in Fig. 1 the evolution of muconic acid and Fe(II) concentration with time corresponding to experiments of TiO_2 and/or Fe(III) photocatalytic oxidations are presented. A previous run with 100 mg L^{-1} of TiO_2 in the dark revealed no adsorption at all of muconic acid on TiO_2 surface. As it is seen from Fig. 1 pH has a negative effect on TiO_2 /UVA degradation of MUC. Also, at pH 3, 50 mg L^{-1} of TiO_2 are needed to give similar results than Fe(III) photocatalytic oxidation of MUC in the presence of $5 \times 10^{-5} \text{ M}$ (2.8 mg L^{-1}). Then, Fe(III) photocatalytic process is a potential oxidation process that deserves some studies compared to TiO_2 photocatalysis since this latter process presents an important drawback: the separation of very finely titania powder from the water. On the other hand, as shown in Fig. 1 and Table 1, initial removal and formation rates of MUC and Fe(II), respectively, in the presence of 10 mg L^{-1} TiO_2 and $5 \times 10^{-5} \text{ M}$ [Fe(III)], were higher than the sum of the rates of both systems. This suggests the development of some sort of synergism between both systems. This phenomena could be due to the activity of Fe(III) as acceptor of promoted electrons, through reaction (7), when TiO_2 is irradiated, in a similar way of the role of oxygen or hydrogen peroxide in reactions (6) and (11). In this way electron-hole recombination is avoided and the activity of TiO_2 is improved [26–28]. Furthermore, if hydrogen peroxide is formed, it can react with Fe(II) (Fenton reaction) to yield more hydroxyl radicals:



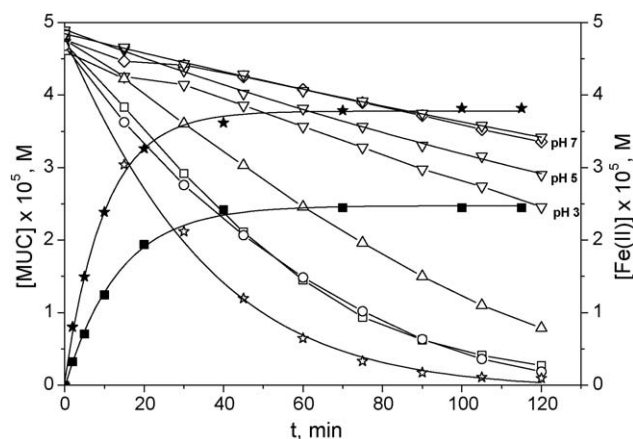


Fig. 1. Effect of TiO_2 and Fe(III) photocatalytic oxidations on the muconic acid removal rate through photocatalytic oxidation. Changes of MUC (open symbols) and Fe(II) (solid symbols) concentrations with time. Conditions: $[\text{MUC}]_0 = 5 \times 10^{-5} \text{ M}$; $I_0 = 7.33 \times 10^{-7} \text{ Einstein s}^{-1}$; $\text{HClO}_4/\text{ClO}_4^-$ pH 3 (except where indicated); ionic strength: 0.03 M ; $T = 25^\circ \text{C}$; oxygen aeration. TiO_2 photocatalytic oxidation: $[\text{TiO}_2]$, mg L^{-1} : (\diamond) 5; (∇) 10; (\triangle) 25; (\circ) 50; Fe(III) photocatalytic oxidation: (\square , \blacksquare) $[\text{TiO}_2] = 0 \text{ mg L}^{-1}$ and $[\text{Fe(III)}]_0 = 5 \times 10^{-5} \text{ M}$ (2.8 mg L^{-1}); (\star , \blackstar) $[\text{TiO}_2] = 10 \text{ mg L}^{-1}$ and $[\text{Fe(III)}]_0 = 5 \times 10^{-5} \text{ M}$ (2.8 mg L^{-1}).

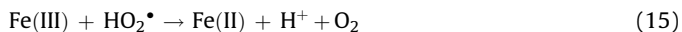
Table 1

Initial removal rate of muconic acid and Fe(II) formation rate in the presence and absence of catalysts^a.

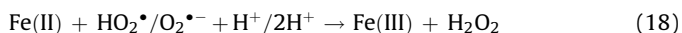
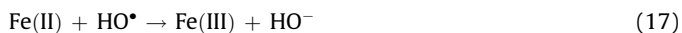
Catalyst and concentration	$-r_{\text{MUC}0}$ ($\times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}$)	$r_{\text{Fe(II)}0}$ ($\times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}$)
$[\text{Fe(III)}]_0 5 \times 10^{-5} \text{ M}$	3.61×10^{-8}	7.86×10^{-8}
$[\text{TiO}_2] 10 \text{ mg L}^{-1}$	1.06×10^{-8}	–
$[\text{Fe(III)}]_0 5 \times 10^{-5} \text{ M}$ and $[\text{TiO}_2] 10 \text{ mg L}^{-1}$	6.40×10^{-8}	1.94×10^{-7}

^a $[\text{MUC}]_0 = 5 \times 10^{-5} \text{ M}$, pH 3, $T = 25^\circ \text{C}$, air bubbling.

Therefore, when TiO_2 is present Fe(II) is being formed from different ways: the photoreduction of Fe(OH)^{2+} (reaction (1)), the reduction of Fe(III) when acts as electron trapping (reaction (7)), and its reduction through reaction with hydroperoxide and/or superoxide ion radicals formed through reaction (6) and equilibrium (8):



Regardless of the presence of TiO_2 , in Fig. 1 it is observed that Fe(II) concentration reaches a stationary value after a given reaction time. Since this steady Fe(II) concentration is always lower than the starting Fe(III) concentration, the oxidation of Fe(II) through reaction (14) or through reactions with HO^\bullet , $\text{O}_2^{\bullet-}/\text{HO}_2^\bullet$ radicals and oxygen:



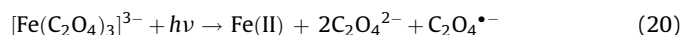
should be considered, although the latter has a low rate constant at the conditions applied in this work [8].

According to the results obtained in this work, the higher efficiency of the $\text{Fe(III)}/\text{UVA}$ system compared to that of TiO_2/UVA system to eliminate MUC from water could be not only due to the different HO^\bullet radical formation quantum yields in both systems but also to the influence of the nature of intermediates formed. Thus, Zazo et al. [22] reported the formation of maleic, fumaric, malonic,

acetic, formic and oxalic acids during the Fenton oxidation of muconic acid. These authors also observed that maleic and malonic acids were oxidized to yield formic, acetic and oxalic acids with the two latter being refractory to further oxidation (likely due to the low rate constant of their reaction with hydroxyl radicals [29]). Therefore, during muconic acid photocatalysis formation of carboxylic acids able to complex Fe(III) (i.e. case of oxalic acid) and their further photoreduction would favour the generation of free radicals and, eventually, a high mineralization level as Franch et al. reports [30].

3.1.1. Effect of carboxylic acids on muconic acid degradation rate by UVA/ Fe(III) system

Ferrioxalate complex is undoubtedly the most studied ferri-complex that photolysis with a quantum yield higher than that of Fe(III) itself to generate hydroxyl radicals. This complex photo-reduces and decarboxylates in the presence of UVA-visible light with 1.2 mol per photon of quantum yield, in terms of Fe(II) formation, through reactions:

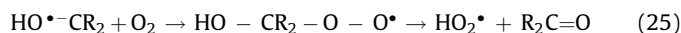


If equilibrium (8) and reactions (9), (10), (14) and (18) are considered, reactions (20)–(22) lead to hydrogen peroxide and hydroxyl radical formation [31–33].

In this work, oxalic as well as citric, maleic, malic, malonic, succinic and tartaric acids were investigated.

3.1.1.1. Oxidation in the presence of citric, tartaric or oxalic acids. Fig. 2 shows, as example, the time evolution of muconic acid remaining concentration as well as Fe(II) concentration corresponding to Fe(III) photocatalytic experiments in the presence and absence of citric acid (CIT).

Ferric citrate photolysis has been studied in detail by different authors [13,28,34]. Main steps of free radical generation are [28]:



where $\text{CIT} = \text{HO}-\text{CR}_2-\text{COO}$, and $\text{R} = -\text{CH}_2\text{COOH}$, so $\text{R}_2\text{C}=\text{O}$ is acetonedicarboxylic acid (3-oxoglutaric acid) that can further be decomposed to acetone and CO_2 ([28] and references therein).

From Fig. 2 it is seen that the presence of citric acid allows high oxidation rates of muconic acid although rate differences are low especially for citric acid concentrations lower than 10^{-4} M . When the concentration of citric acid is 10^{-3} M an induction period is observed in the muconic acid disappearance rate. This period can be due to the development of competitive reactions of generated radicals with intermediates of ferric citrate decarboxylations and/or with the Fe(II) formed. However, after the initial induction period, conversion of muconic acid is even higher than that achieved in the presence of smaller concentrations of citric acid. On the other hand, from Fig. 2 it is also observed two different trends on the evolution of Fe(II) concentration with time, depending on the presence/absence of citric acid. Thus, in the absence of citric acid, Fe(II) formed from Fe(III) photolysis continuously increases with time to finally reach a stationary concentration value of approximately $2.5 \times 10^{-5} \text{ M}$ which is half the value of the initial concentration of Fe(III) in the experiment. This means that Fe(II) is partly oxidized to yield Fe(III) and a redox process is finally developed.

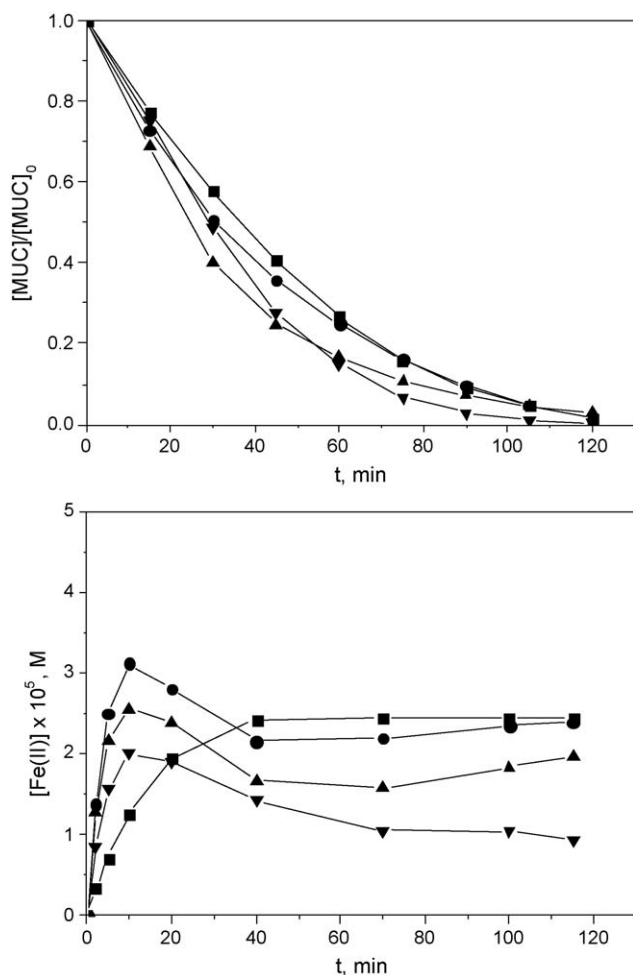


Fig. 2. Effect of initial citric acid concentration on the muconic acid removal rate through Fe(III)/photocatalytic oxidation. Changes of MUC (top) and Fe(II) (bottom) concentrations with time. Conditions: $[\text{Fe(III)}]_0 = 5 \times 10^{-5} \text{ M}$; $[\text{MUC}]_0 = 5 \times 10^{-5} \text{ M}$; $I_0 = 7.33 \times 10^{-7} \text{ Einstein s}^{-1}$; $\text{HClO}_4/\text{ClO}_4^-$ pH 3, ionic strength: 0.03 M; $T = 25^\circ \text{C}$; oxygen aeration; $[\text{CIT}]_0$, M: (■) 0; (●) 5×10^{-5} ; (▲) 10^{-4} ; (▼) 10^{-3} M.

In the presence of citric acid, Fe(II) concentration–time curve (see Fig. 2) presents up to three or four different reaction periods, depending on the initial citric acid concentration. Similar results were observed when the Fe(III) photocatalytic oxidation was carried out in the presence of oxalic (OXAL) or tartaric acids (TART): a common initial reaction period where the Fe(II) concentration increases with time to reach a maximum value. A second decreasing Fe(II) concentration period also presents regardless of citric acid concentration. A third period where no variation in Fe(II) concentration is observed and a fourth period where Fe(II) concentration starts to slightly increase. This latter period only develops for the lowest concentrations of citric acid tested. It is also observed that the maximum Fe(II) concentration reached in the initial reaction period significantly depends on the citric acid concentration. Thus, the higher the citric acid concentration the lower the maximum Fe(II) concentration (see later). In any case, regardless of citric acid concentration present in the water, the initial rate of Fe(II) formation during this first period is always higher than that measured in the absence of citric acid. This suggests the formation of a Fe(III)–citric acid complex (a ferrictrate complex) that photolyses even better than Fe(III) alone to yield free radical species and Fe(II). The formation of this complex was confirmed by measuring the absorbance of solutions of Fe(III) and citric acid both separately and in a mixture of them.

Thus, at wavelengths above 350 nm (that correspond to the emission spectrum of the lamps used) the absorbance of a Fe(III) and citric acid mixture was always higher than that of the sum of the absorbances of Fe(III) and citric acid solutions separately measured. Also, from the results obtained the quantum yield of the ferrictrate complex photolysis at 365 nm, in terms of Fe(II) formation, varied from 0.34 to 0.55 mol per photon in the presence of citric acid concentrations between 10^{-3} and $5 \times 10^{-5} \text{ M}$, respectively, and $5 \times 10^{-5} \text{ M}$ Fe(III) concentration. In the absence of citric acid, the quantum yield of Fe(III) photolysis was found to be 0.1 mol per photon at 365 nm. In the case of oxalic and tartaric acids similar effects were observed. Also, in these cases, Fe(III) carboxylate complexes photolyse with higher quantum yields than Fe(III) itself. Thus, for a 10^{-4} M carboxylic acid concentration and $5 \times 10^{-5} \text{ M}$ Fe(III) concentration the quantum yield at 365 nm of the corresponding complex photolysis was 0.99 and 1.10 mol per photon for the cases of ferrioxalate and ferritartrate complexes, respectively.

The negative effect observed of the concentration of citric acid on the maximum Fe(II) concentration attained (see Fig. 2) can be attributed to competitive reactions between the Fe(II) formed and the oxidant species generated in the ferrictrate photolysis at such conditions. This would explain the induction period observed in the removal rate of MUC. These oxidant species are responsible of the decrease in the Fe(II) concentration with time observed during the second period that also oxidize Fe(II) to regenerate Fe(III). The third reaction period is likely due to a redox process where the ferrictrate has already disappeared and Fe(II) oxidation and Fe(III) photolysis reaction keep constant the Fe(II)/(III) species concentrations. This is only observed when the concentration of citric acid was low (lower than 10^{-4} M). Finally, in the fourth reaction period also observed for low citric acid concentration, Fe(II) concentration increases again as a consequence of the absence of ferrictrate complex that has also been consumed by the action of free radicals. The results obtained when oxalic or tartaric acid was present in water were always similar although oxalic acid resulted the most recommended acid to accelerate the muconic acid oxidation rates (see later comparison of the effects of carboxylic acids).

3.1.1.2. Oxidation in the presence of maleic acid or succinic acids. A second series of muconic acid Fe(III) photocatalytic oxidations were carried out in the presence of different concentrations of maleic acid and succinic acid. However, in these systems, the presence of maleic acid yielded lower muconic acid oxidation rates than in the maleic acid free photocatalytic oxidation. Also, the evolution of Fe(II) concentration with time was independent on the presence or absence of maleic acid in solution. On the other hand, the addition of succinic acid did not cause any effect on muconic acid degradation nor Fe(II) formation. From these results it is deduced that maleic or succinic acid do not form any complex with Fe(III) which was confirmed from the absorbance of solutions of Fe(III)–maleic or succinic acid mixtures and the sum of absorbances of their aqueous solutions separately measured. In this case, no differences were observed in the absorbances from these solutions. Inhibition of muconic acid oxidation when maleic acid is present is undoubtedly due to the competitive effect of both organics for the free radicals formed in the direct photolysis of Fe(III). This seems to be a logical consequence of the presence of carbon double bonds in their molecules that make their reaction with HO radicals very fast (the rate constant of the HO^\bullet –maleic reaction at pH 4–10.5 is approximately $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as Buxton et al. reported [29]).

3.1.1.3. Oxidation in the presence of malic or malonic acids. Fig. 3 shows the effect of the presence of malic and malonic acids on the oxidation rate of muconic acid and the evolution of Fe(II)

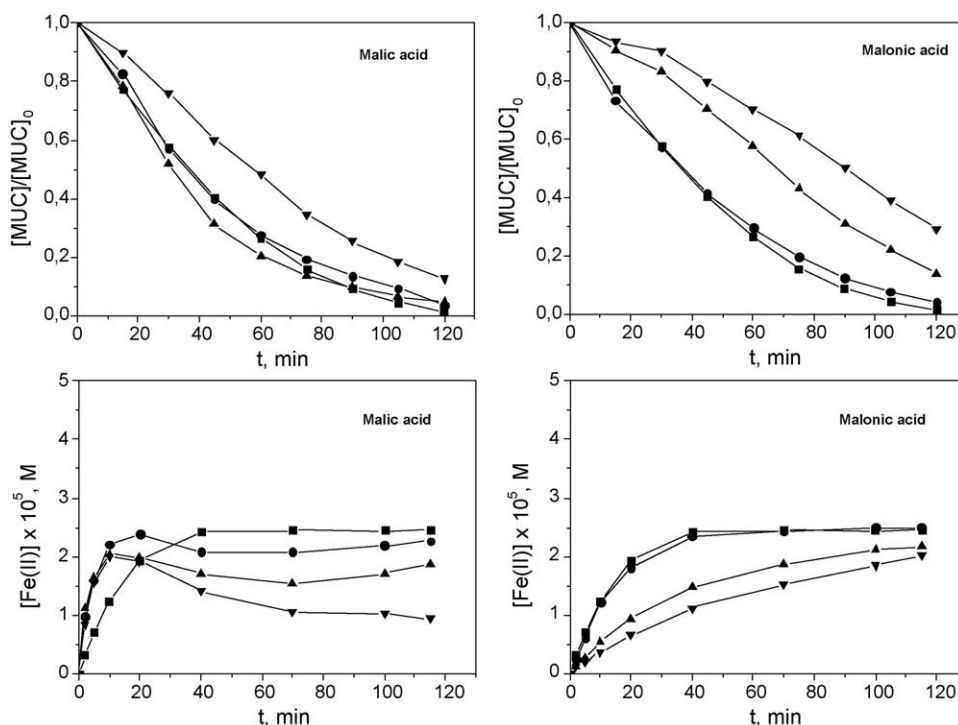


Fig. 3. Effect of initial malic acid (left) and malonic acid (right) concentrations on the muconic acid removal rate through Fe(III)/photocatalytic oxidation. Changes of MUC (top) and Fe(II) (bottom) concentrations with time. Conditions: $[\text{Fe(III)}]_0 = 5 \times 10^{-5} \text{ M}$; $[\text{MUC}]_0 = 5 \times 10^{-5} \text{ M}$; $I_0 = 7.33 \times 10^{-7} \text{ Einstein s}^{-1}$; $\text{HClO}_4/\text{ClO}_4^-$ pH 3, ionic strength: 0.03 M; $T = 25^\circ \text{C}$; oxygen aeration; symbols: left plots: $[\text{MALI}]_0$, M: (■) 0; (●) 5×10^{-5} ; (▲) 10^{-4} ; (▼) 10^{-3} , right plots: $[\text{MALO}]_0$, M: (■) 0; (●) 10^{-5} ; (▲) 5×10^{-5} ; (▼) 10^{-4} M.

concentration during the Fe(III) photocatalytic process. As it can be seen from Fig. 3, concentrations of malic acid (MALI) up to 10^{-4} M exert a slight positive effect on muconic acid removal but higher concentrations clearly inhibit the degradation rate. From this figure it is seen that the evolution of Fe(II) concentration with time when malic acid was present is similar to the case of the carboxylic acids (such as citric acid) that form ferricarboxylate complexes. On the other hand, the effect of malonic acid (MALO) is negative. In this case, as it can be deduced from Fig. 3, the higher the concentration of malonic acid the higher the inhibition rate of muconic acid oxidation. Moreover, Fig. 3 shows that the concentration of Fe(II) is continuously increasing with time, regardless of malonic acid concentration (there are no different trends in Fe(II) concentration as it happens in the presence of citric, oxalic and malic acids), but the increasing concentration of malonic acid yields decreasing concentrations of Fe(II).

As far as the formation of ferricarboxylate complexes is concerned, literature reports that malonic acid forms complexes with Fe(III) [35]. However, the presence of malonic acid is detrimental for the oxidation rate of muconic acid which seems to be in contradiction with the results obtained with other carboxylic acids that complex Fe(III). Then, the absorbance of solutions containing a mixture of Fe(III) and malonic acid and the sum of absorbances of individual solutions of Fe(III) and malonic acid were measured. As shown in Fig. 4 for wavelengths above 320 nm the absorbance of the mixture was lower than that of the sum. Then, the ferrimalonate complex does not absorb in the UVA region and, as a consequence, is unable to photolyse and decompose in Fe(II) and free radicals. This would explain the inhibition of muconic acid oxidation when malonic acid is present as well as the low concentrations of Fe(II) in the water. Malonic acid acts, therefore, as inhibitor of muconic acid photocatalytic process.

Malic acid also forms a ferric complex that absorbs radiation at wavelengths above 320 nm as experimentally checked in this

work. Then, the ferrimalate complex photolytically decomposes to yield Fe(II) and free radicals and its presence should be beneficial for the removal of muconic acid from water. However, as Fig. 3 shows concentrations of malic acid higher than 10^{-4} M clearly inhibit the oxidation rate. A possible explanation of these results can be attributed to the appearance of malonic acid as intermediate during malic acid decarboxylation as Danion et al. [36] report in their studies on the TiO_2 photocatalytic oxidation of malic acid. Thus, once malonic acid is formed, Fe(III) also reacts with it to yield the photocatalytically inactive, in the UVA region, ferrimalonate complex that slows down the generation of free radicals as commented above. This would explain the inhibiting character of malic acid to slow down the oxidation of muconic acid in spite of forming a photocatalytic active ferric complex.

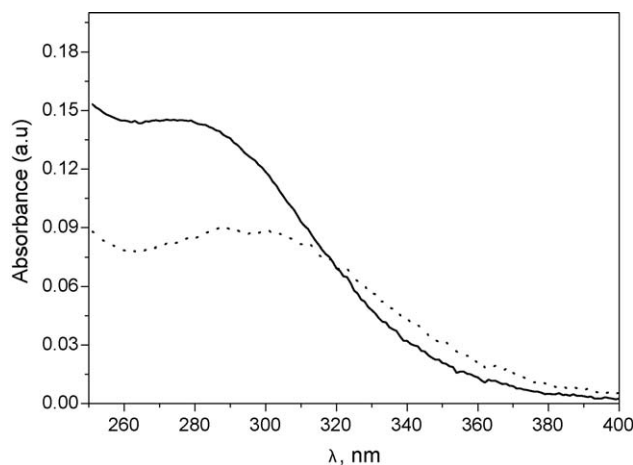
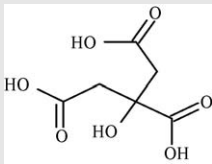
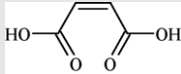
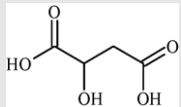
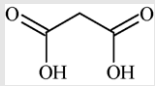
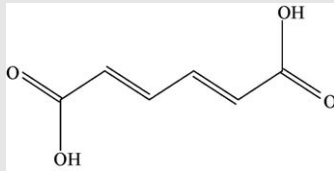
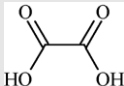
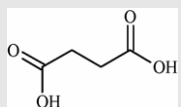
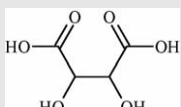


Fig. 4. Absorbances at different wavelengths of Fe(III)-malonic acid. Dotted line: sum of absorbances of Fe(III) and malonic acid separate solutions. Continuous line: absorbance of a mixture of Fe(III) and malonic acid.

Table 2Structure of carboxylic acids, formation of Fe(III) complexes, quantum yield of Fe(II) formation and muconic acid half life ($I_{365\text{ nm}} = 7.33 \times 10^{-7}$ Einstein s^{-1} , pH 3, 20 °C).

Carboxylic acid	Fe(III)-complex/UV-A absorbance	$(\Phi_{\text{Fe(II)-365 nm}})_0^a$ (mol Einstein $^{-1}$)	MUC half life a (min)
Citric acid ($\text{p}K_{\text{a}1} = 3.09$; $\text{p}K_{\text{a}2} = 4.75$; $\text{p}K_{\text{a}3} = 5.41$) 	Yes/yes	0.589	25
Maleic acid ($\text{p}K_{\text{a}1} = 1.93$; $\text{p}K_{\text{a}2} = 6.58$) 	No	0.099	66
Malic acid ($\text{p}K_{\text{a}1} = 3.4$; $\text{p}K_{\text{a}2} = 5.11$) 	Yes/yes	0.510	31
Malonic acid ($\text{p}K_{\text{a}1} = 2.85$; $\text{p}K_{\text{a}2} = 5.69$) 	Yes/no	0.026	90
<i>t,t</i> -Muconic acid ($\text{p}K_{\text{a}1} = 2.7$; $\text{p}K_{\text{a}2} = 4.7$) 	No	0.101	37
Oxalic acid ($\text{p}K_{\text{a}1} = 1.23$; $\text{p}K_{\text{a}2} = 4.19$) 	Yes/yes	0.993	13
Succinic acid ($\text{p}K_{\text{a}1} = 4.16$; $\text{p}K_{\text{a}2} = 5.61$) 	No	0.096	39
Tartaric acid ($\text{p}K_{\text{a}1} = 3.03$; $\text{p}K_{\text{a}2} = 4.45$) 	Yes/yes	1.102	26
None		0.062 b	–

^a Obtained in this work when $[\text{Fe(III)}]_0 = 5 \times 10^{-5}$ M; $[\text{MUC}]_0 = 5 \times 10^{-5}$ M, 10^{-4} M for the rest of acids;^b Reported to be 0.07 by Benkelberg and Warneck [37].

3.1.2. Comparison between systems

From the results obtained it is deduced that all carboxylic acids able to complex Fe(III) and form ferricarboxylates, except the case of malonic acid, allow, depending on their concentration, significant increases of muconic acid oxidation rates. Then, it could be interesting to establish some relationship between the molecular structure of the acids, their capacity to form

ferricarboxylate complexes, the ability to photodecompose in Fe(II) and free radicals and the removal rate of MUC. Thus, Table 2 presents these characteristics as a function of the initial quantum yield of Fe(II) generation and MUC half life. Although studies with a high number of carboxylic acids are recommended, from data shown in Table 2 the following conclusions can be drawn:

1. Carboxylic acids with a HO group in their molecule (hydroxyl or carboxyl) in α position with respect to one carboxylic acid group (this is the case of oxalic, citric, malic and tartaric acids) form ferricarboxylate complexes that absorb UVA radiation.
2. Carboxylic acids with a HO group in β position with respect to one carboxylic acid group (case of malonic acid) form ferricarboxylate complexes that do not absorb UVA radiation.
3. Carboxylic acids that do not fulfil conditions 1 or 2 do not form ferricarboxylate complexes (case of maleic, muconic and succinic acids).
4. In the absence of any carboxylate, the initial Fe(III) photoreduction quantum yield at 365 nm resulted to be 0.062 mol per photon, closed to 0.07 Benkelberg and Warneck [37] reported. In the presence of MUC, that does not form any ferric complex, the quantum yield increases to 0.100, which suggests MUC acts as hydroxyl radical scavenger avoiding the oxidation of Fe(II).
5. Accordingly to our results, the efficiency of ferricarboxylate complexes to remove MUC presents the following order: Fe(III)–OXAL > Fe(III)–TART \approx Fe(III)–CIT > Fe(III)–MALI > Fe(OH)²⁺. Notice that this sequence does not exactly match the light absorbance at 365 nm at pH 3 of ferricarboxylate complexes formed that has the following order: citric acid (900 M⁻¹ cm⁻¹, [28]) > oxalic acid (800 M⁻¹ cm⁻¹, this work) > tartaric acid (350 M⁻¹ cm⁻¹, this work) > malic acid (270 M⁻¹ cm⁻¹, this work) > Fe(OH)²⁺ (250 M⁻¹ cm⁻¹, [1]). In this work, molar absorptivities were obtained measuring the absorbance at 365 nm of solutions of different ferricarboxylate concentration and working in an excess of carboxylate with a constant value of 4 for the [carboxylate]:[Fe(III)] ratio. The stoichiometry of carboxylate:Fe(III) complexes was considered to be 1:1 for tartrate and malate complexes and 3:1 for ferrioxalate.

The following reasons can explain these results: (a) the different quantum yield that can be measured from the Fe(II) formation rate. Thus, at 365 nm radiation, in the presence of

5×10^{-5} M for MUC and Fe(III) and 10^{-4} M complexing agent, the quantum yields of Fe(II) formation corresponding to the photolysis of Fe(OH)²⁺ (absence of ligand), ferric citrate, ferrioxalate, ferritartrate and ferrimalate complexes were found to be 0.10, 0.59, 0.99, 1.10 and 0.51 mol per photon, respectively (see Table 2); (b) the stoichiometry of the ferricarboxylate complexes that was also different. For example, to form 1 mol of the ferrioxalate and ferric citrate complexes from 1 atom of Fe(III) 3 mol of oxalic acid and 1 mol of citric acid were needed, respectively. This means that starting with the same initial concentrations of Fe(III) and citric or oxalic acid (let us say, 5×10^{-5} M) concentrations of ferric citrate and ferrioxalate complexes were 5×10^5 and 1.7×10^{-5} M, respectively, and (c) also important is to consider that intermediate compounds formed in each process are different and hence their competition for free radicals. For example, in the case of oxalic acid there are only final unreactive products: water and carbon dioxide, while the other ferricarboxylates give rise to intermediates that also consume free radicals or even form other ferric complexes that can undergo photolysis as well.

Another interesting aspect to deal with is the change of initial quantum yield for Fe(II) generation observed as a function of the presence/absence of MUC and the initial organic acid ligand:Fe(III) ratio. Thus, as it is shown in Fig. 5, regardless of the type of ferricarboxylate tested, the presence of MUC exerts a positive effect on the quantum yield in different systems. Since MUC does not form Fe(III) complexes these results suggest that MUC acts as a free radical scavenger by inhibiting radical-Fe(II) reaction to regenerate Fe(III). Therefore, the most accurate value of the quantum yield can be obtained when some free radical scavenger, such as MUC, is present.

Also, from Fig. 5 one can observe some negative effect of the initial ligand–Fe(III) ratio on the Fe(II) quantum yield. However, this should be rather interpreted as the result of photogenerated Fe(II) oxidation to Fe(III) due to a high free radical concentration present in water at these conditions.

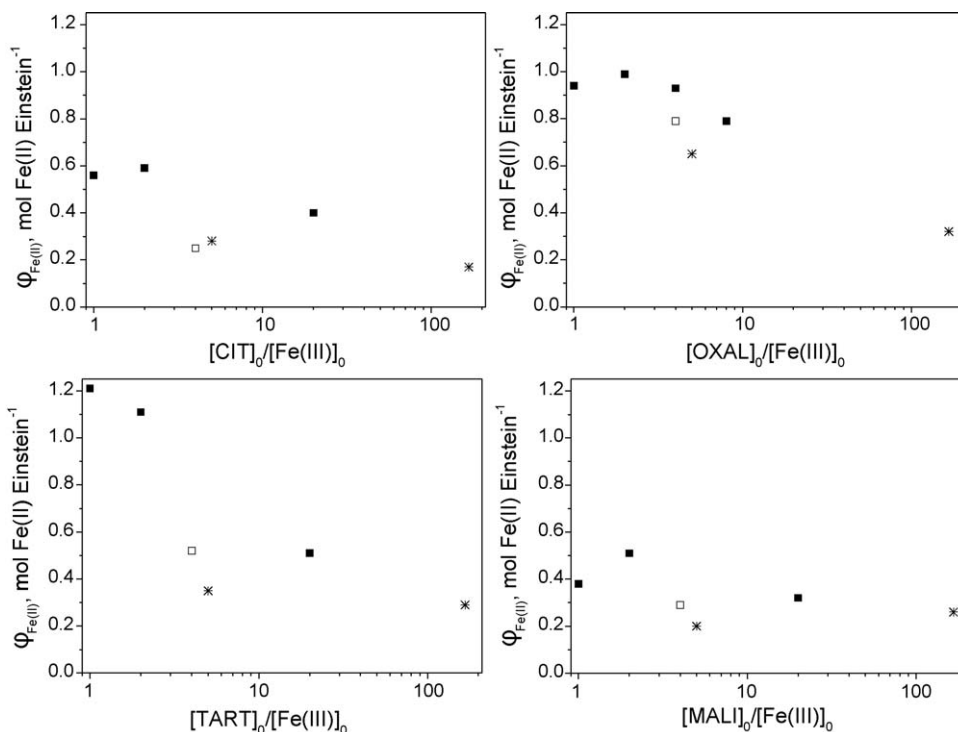


Fig. 5. Variation of Fe(II) formation quantum yield with the carboxylic acid/Fe(III) ratio. Symbols: in the presence 5×10^{-5} M muconic acid (■); in the absence of any other organic compound: (□) this work; (*) Abrahamson et al. [34].

Table 3Experimental conditions of solar photocatalytic runs^a.

Date	Run	Weather conditions	T^b (°C)	$I_{365\text{ nm}}^b$ ($\mu\text{W cm}^{-2}$)
06/10/2006	A		26	1900
26/10/2006	B		21	1300
16/11/2006	C		17	320
14/12/2006	D		17	1760
29/01/2007	E		10.5	500
13/02/2007	F		16.5	260
16/04/2007	G		15	1900
11/05/2007	H		26	2000
25/06/2007	I		26	2460
24/07/2007	J		29	2290
	J.1 ([OXAL] ₀ = 10 ⁻⁴ M)			
	J.2 ([TART] ₀ = 10 ⁻⁴ M)			
	J.3 ([CIT] ₀ = 10 ⁻⁴ M)			

^a [MUC]₀ = 5 × 10⁻⁵ M; [Fe(III)]₀ = 5 × 10⁻⁵ M; pH 3 HClO₄/ClO₄⁻ 0.03 M.^b Average value during exposition time.

3.2. Solar light as source of photons

A more environmentally friendly process is the use of solar light to photodecompose ferricarboxylates or initiate the Fe(III) photodecomposition in free radicals. In fact, solar light covers the continuous spectrum of radiation till 320 nm as a difference from black light that mainly emits 350–390 nm radiation. This circumstance acts in a favourable way in the photocatalytic systems treated since the quantum yield of some of the ferricarboxylates studied could be higher at wavelengths below 350 nm as happens for the Fe(OH)²⁺ species [1]. It is evident that the intensity of the solar light is also an important factor to increase the photocatalytic rate of organic oxidation in water. Therefore, the season of year, the weather conditions and the geographic situation of the photoreactor (latitude and length) are key factors that affect the photocatalytic oxidation rates of organics when solar light is being used. In this work, a series of muconic acid Fe(III) solar photocatalytic oxidation experiments were carried out from October 2006 to July 2007. Table 3 presents the weather conditions and the average intensity of UVA solar radiation at 365 nm corresponding to the days when experiments were carried out. The geographical coordinates correspond to the city of Badajoz (38° 53' north latitude, 6° 58' west length). In Fig. 6 the evolution of muconic acid concentration with time corresponding to these experiments is shown. As can be observed, weather conditions rather than season of the year were the key factor since, for example, 50% removal of muconic acid was achieved in 17 min in run J (July, sunny day, 29 °C, 2290 μW cm⁻²

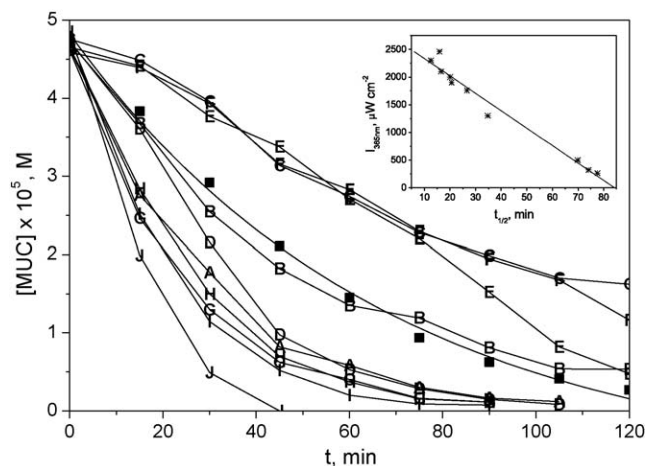


Fig. 6. Fe(III)/solar photocatalytic oxidation of muconic acid. Variation of muconic acid concentration with time. Effect of year season and weather conditions. Conditions: [Fe(III)]₀ = 5 × 10⁻⁵ M; [MUC]₀ = 5 × 10⁻⁵ M; HClO₄/ClO₄⁻ pH 3, ionic strength: 0.03 M; other conditions see Table 2, runs A–J. Symbols (■) same conditions but with black light. Insert: relationship between UV-A solar intensity and muconic acid half life.

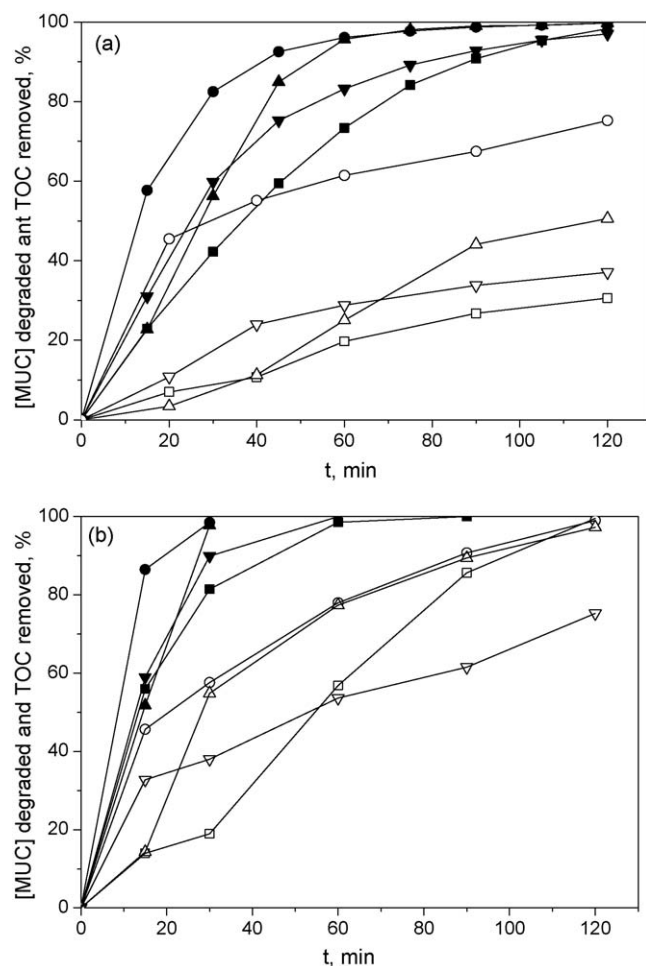


Fig. 7. Percentage changes with time of muconic acid concentration (solid symbols) and TOC (open symbols). Top plot (a): with black light. Bottom plot (b): with solar light. Effect of the presence and type of carboxylic acid. Experimental conditions in Table 2, runs: J–J.3; (■, □): absence of complexing carboxylate; (●, ○): [OXAL]₀ = 10⁻⁴ M; (▲, △): [TART]₀ = 10⁻⁴ M; (▼, ▽): [CIT]₀ = 10⁻⁴ M.

$I_{365\text{ nm}}$), 30 min in run D (December, sunny day, 17 °C, 1760 $\mu\text{W cm}^{-2}$ $I_{365\text{ nm}}$) and more than 60 min in runs C, E and F (rainy and/or cloudy days, 10.5–17 °C, 260–500 $\mu\text{W cm}^{-2}$ $I_{365\text{ nm}}$). As it can also be seen in Fig. 6 (insert) a linear relationship ($r^2 = 0.971$) between the average UV-A intensity of solar radiation and muconic acid half life was found.

3.3. Comparison between black light lamps and solar photocatalytic processes

The most important objective of chemical or photochemical oxidation of organics in water is mineralization. Thus, Fig. 7 shows the evolution of the percentage of MUC and total organic carbon (TOC) removed with time corresponding to muconic acid Fe(III) photochemical oxidation experiments in the absence/presence of citric, tartaric and oxalic acids, with black light (Fig. 7a) and solar light (Fig. 7b). As it can be seen from Fig. 7a, after 2 h treatment, the presence of citric, tartaric and oxalic acid, at a concentration of 10^{-4} M, approximately, allows 37, 51 and 75% removal of TOC, respectively, and 31% in the absence of any ferricboxylate. With solar light (Fig. 7b, experiences J–J.3 in Table 3, July 24, 2007, a sunny day with 29 °C and 2290 $\mu\text{W cm}^{-2}$ $I_{365\text{ nm}}$), the presence of oxalic acid allows the highest photocatalytic oxidation rates and total conversion of muconic acid was achieved in about 30 min when oxalic or tartaric acids was present. Finally, as far as the variation of TOC percentage removal with time is concerned, also from Fig. 7b it is seen that after 2 h reaction, 100% TOC removal is reached regardless of the type of carboxylic acid added to the water except for Fe(III)–citric acid photocatalytic experiment. In this case the percentage was 75% which is related to the higher complexity of the CIT molecule compared to the rest of carboxylic acids as shown in Table 2.

4. Conclusions

Depending on the radiation source the following conclusions have been reached in this work.

4.1. Black light lamps experiments

At the conditions investigated Fe(III) photocatalytic oxidation results better than TiO_2 photocatalytic oxidation to degrade muconic acid from water. The removal rate of muconic acid is significantly increased when photooxidation is carried out in the presence of carboxylic acids with one HO group in the α position with respect to the carboxylic acid group. Thus, in the presence of oxalic, malic, citric and tartaric acids some ferricboxylate complex is formed that absorbs UVA radiation and photodecomposes in Fe(II) and free radicals that accelerate the oxidation rate. Some other carboxylic acids exert, however, a negative effect on the muconic acid removal rate. These are those acids that do not form ferriccomplexes and compete for the free radicals (case of maleic acid) or do form ferricboxylate complexes that do not absorb UVA radiation (case of malonic acid) and, hence, diminish the photoefficiency of the system.

4.2. Solar light experiments

There is a direct dependency between the weather conditions and the rate of muconic acid oxidation with the Fe(III)–solar light

system. Thus a linear relationship was found between the average intensity of the solar radiance (measured at 365 nm, $I_{365\text{ nm}}$) and the muconic acid half life. The presence of oxalic, citric and tartaric acids during the Fe(III)–solar light oxidation of muconic acid significantly increased the rate of oxidation of this acid reaching TOC removal percentages higher than 75% after 2 h photoreaction in all the cases.

Further research on the effects of natural organic matter (such carboxylic acids), metal catalysts, whether in solution or as solids, and solar light on the removal of specific organic contaminants is now in progress and will be the subject of future publications.

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